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RESEARCH ARTICLE

Synthesis and Characterization of Bidentate (P^N)Gold(III) Fluoride Complexes: Reactivity Platforms for Reductive Elimination Studies

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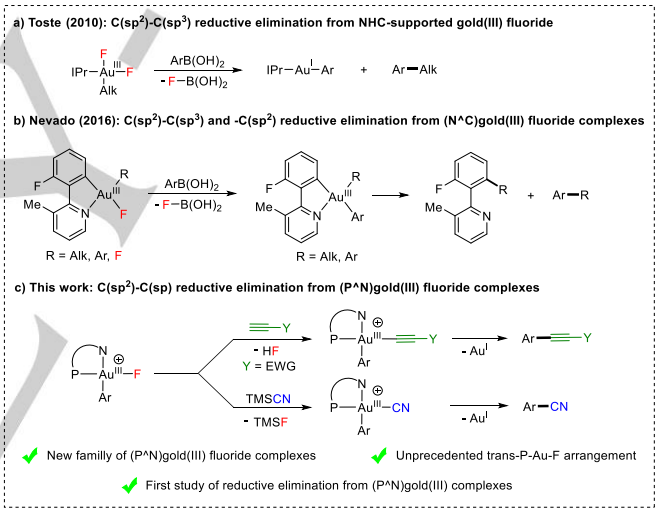
Abstract: A new family of cationic, bidentate (P^N)gold(III) fluoride complexes has been prepared and a detailed characterization of the gold-fluoride bond has been carried out. Our results correlate with the observed reactivity of the fluoro ligand, which undergoes facile exchange with both cyano and acetylene nucleophiles. The resulting (P^N)arylgold(III)C(sp) complexes have enabled the first study of reductive elimination on (P^N)gold(III) systems demonstrating that C(sp^2)-C(sp) bond formation occurs at higher rates than those reported for analogous phosphine-based monodentate systems.

Introduction

Late transition metal fluorides raise interesting questions in bonding and reactivity compared to their heavier halide analogues.[1] Highly oxidized palladium and nickel fluoride complexes have been isolated and intensively studied because of their crucial role in C−H activation, fluorination, oxidation, and cross-coupling reactions.[2,3] In contrast, and despite the emergence of gold(I)/gold(III) catalysis as a complementary tool in this context,[4] gold(III) fluoride complexes have remained largely unexplored until recently. Numerous gold-catalyzed oxidative couplings forging C(sp^2)-C(sp^2) and C(sp^2)-C(sp^3) bonds employed electrophilic fluorinating reagents to enable gold(I)/gold(III) redox cycles and invoked gold(III) fluorides as key intermediates.[5] However, isolated organogold fluoride complexes are scarce as they represent an extreme mismatched pair according to the HSAB theory.[6] Seminal work by Toste on the oxidation of (NHC)gold(I)alkyl species with XeF_2 resulted in the isolation of the first gold(III) fluorides *cis*-[(NHC)Au^{III}AlkylF$_2$]. These complexes react with boronic acids enabling the formation of C(sp^2)-C(sp^3) bonds (Scheme 1a).[6d] Using a complementary approach devoid of oxidizing conditions, our group has also prepared and characterized a set of novel [(C^N)Au^{III}F$_2$], [(C^N)Au^{III}ArylF] and [(C^N)Au^{III}AlkylF] complexes which, upon transmetallation with organoboron reagents, enabled the study of the C(sp^2)-C(sp^2) and C(sp^2)-C(sp^3) reductive elimination processes (Scheme 1b).[6g]

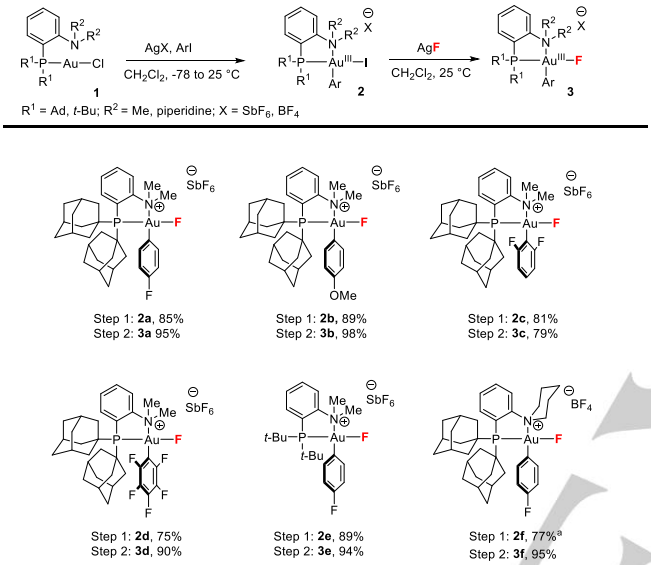


Scheme 1. Synthesis and reactivity of gold(III) fluoride complexes towards C-C bonds formation.

Recent examples focused on the structural characterization of gold(III) fluorides have also been reported by Riedel,[6h, 6i] Menjón[6j] and Dutton,[6k] respectively. Interestingly, and despite these significant advances, the reactivity of gold(III) fluorides in the context of C(sp^2)-C(sp) reductive elimination has not been explored yet even if they have been proposed to be crucial reaction intermediates in this type of C-C bond forming reactions.[5g-i] Herein, we present a new family of bidentate (P^N)arylgold(III) fluorides featuring an unprecedented *trans*-P-Au-F arrangement. A detailed structural and computational characterization of the Au^{III}-F bond has been carried out correlating the ligand exchange ability of the fluoride with both cyano and acetylene nucleophiles. In addition, we present the first study on the C(sp^2)-C(sp) bond forming reductive elimination from (P^N)gold(III) complexes and demonstrate that this process occurs at higher rates than those reported for analogous phosphine-based monodentate systems (Scheme 1c).

Results and Discussion

The synthesis of different arylgold(III) fluorides complexes (**3a-d**) was accomplished from the corresponding (MeDalPhos)gold(I)[7] chloride (**1a**, R^1 = Ad, R^2 = Me) through a two-step process including oxidative addition with Ar-I followed by I/F ligand exchange with AgF in dichloromethane (CH_2Cl_2) at 25 ºC (Scheme 2).[4f, 6g, 8] The complexes were stable in solution for approximately two days at room temperature under inert atmosphere. In order to evaluate steric effects around the metal center, 2-(di-*tert*-butylphosphino)-*N*,*N*-dimethylaniline and 2-(di-1-adamantylphosphino)phenyl-piperidine ligands were employed to synthesize complexes **3e** and **3f** following the same two-step procedure (Scheme 2).



Scheme 2. Synthesis of novel (P^N) arylgold(III) fluoride complexes. See ref. 12 for experimental details. [a]For **3f**, $AgBF_4$ was used instead of $AgSbF_6$ due to the low solubility of the nascent SbF_6 salt in CH_2Cl_2.

Single crystals of **3a**, **3b**, **3d** and **3e** were obtained by slow diffusion of *n*-hexanes into a concentrated CH_2Cl_2 solution of each complex at -30 °C (Figure 1). The analysis of the structures obtained by X-ray diffraction shows that all compounds crystallize as monomeric species in which the metal center has a distorted square planar geometry. The *trans* relationship between P and F, unprecedented for gold(III), was also confirmed by the high $^2J_{P,F}$ coupling constants observed in the $^{31}P\{^1H\}$ ($\delta_P = 71.59$ ppm, d, $^2J_{P,F}$ = 100.5 Hz; for **3a**) and ^{19}F NMR spectra ($\delta_F = -143.8$ ppm, d, $^2J_{P,F}$ = 100.5 Hz; for **3a**).[2i, 8] It is noteworthy that the Au-F distances correlate with the substitution pattern of the aryl ligand: the Au-F bond length increases for electron-deprived compared to more electron-rich counterparts (d_{Au-F} for **3a** (*p*-F): 2.023 Å; **3b** (*p*-OMe): 2.006 Å; **3d** (5F): 2.133 Å) (Figure 1 and Table 1).

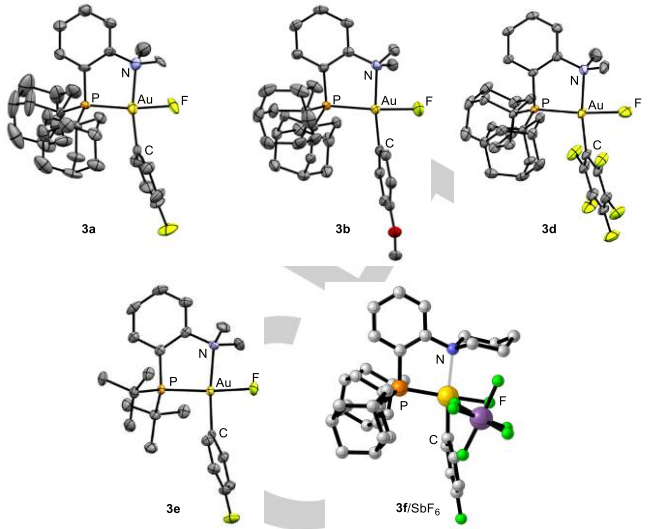


Figure 1. X-ray crystal structures of **3a**, **3b, 3d**, **3e** shown as 50% ellipsoids (H and SbF_6 omitted for clarity). Computed structure of **3f**/SbF_6 (B3LYP, 6-31G(d,p), Au (SDDAll), solvent (smd) =dichloromethane.

Despite numerous attempts, the crystallization of **3f** was not possible due to its lability in solution. In order to obtain further insights, the structure of this complex (together with those of **3a** and **3e** for the sake of comparison) was optimized by DFT calculations. Bond distances and angles calculated for all three compounds **3a**, **3e** and **3f** can be found in Table 1. The distances and angles obtained for the computed structures of **3a** and **3e** deviate minimally from those measured in the crystals (Δd_{max}: 0.07 Å; $\Delta\alpha_{max}$: 2.0 °), thus rendering a comparative analysis with the obtained data for complex **3f** meaningful.

Table 1. Selected X-ray and computed bond distances (Å) and angles (°) for **3a**, **3b**, **3d**, **3e** and **3f**/SbF_6 (B3LYP, 6-31G(d,p), Au (SDDAll), solvent (smd) =dichloromethane.

Angles (°)	3a		3b	3d	3e		3f/SbF_6
	X-ray	DFT	X-ray	X-ray	X-ray	DFT	DFT
N-Au-F	86.1 (4)	88.0	87.5 (1)	88.0 (1)	87.9 (1)	88.3	93.9
C-Au-F	83.7 (5)	84.2	85.6 (1)	83.5 (1)	85.6 (2)	84.3	80.1
P-Au-C	103.1 (4)	102.0	100.9 (1)	102.3 (7)	99.3 (1)	101.4	100.5
Distances (Å)	3a		3b	3d	3e		3f
	X-ray	DFT	X-ray	X-ray	X-ray	DFT	DFT
Au-P	2.278 (3)	2.351	2.299 (1)	2.309 (1)	2.270 (1)	2.344	2.356
Au-F	2.023 (8)	2.033	2.006 (2)	2.133 (2)	2.000 (3)	2.030	2.034

Interestingly, the additional steric hindrance imposed by the piperidine moiety on the N ligand seems to have the strongest influence in disrupting the square planar geometry of the complexes, as reflected on the smaller C-Au-F angle determined for N-piperidine complex **3f** (80.1°) compared to $N(Me)_2$

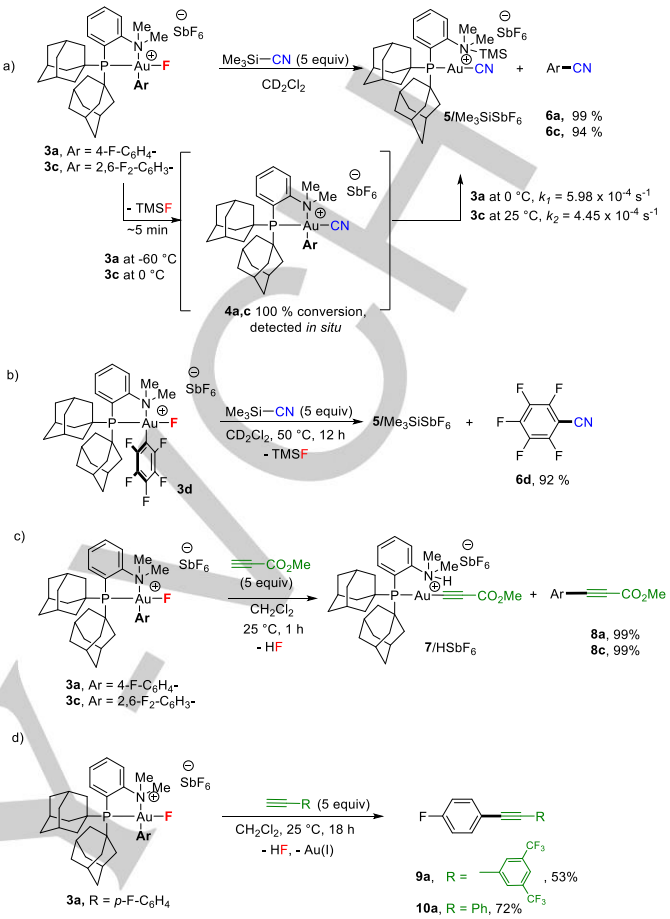
derivatives **3a**: 84.2°(83.7(5)° from X-ray) and **3e**: 84.3°(85.6(2)°) from X-ray) (Table 1). In contrast, the *trans*-($^2J_{P-F}$) coupling constant seems to be much more influenced by the substituents on the P atom with 100.5 and 100.0 Hz values obtained for adamantly-substituted complexes **3a** and **3f** vs. 107.2 Hz measured for *t*Bu-substituted one (**3e**) (Table 2).[9]

Previously, the magnitude of the *trans*-($^2J_{P-X}$) coupling constant in both gold(I) (X = ^{13}C)[10a] and Pd(II) (X = ^{15}N)[10b] complexes has been used to characterize the electronic nature of the metal: typically, larger coupling constants are correlated with higher nuclear charges on the two chelating atoms of the ligands, thus rendering a more electropositive metal center. In the case of complexes **3a**, **3e** and **3f** we can observe how despite the larger $^2J_{P-F}$ observed for *t*Bu$_3$P-ligated complex **3e** (107.2 Hz), the charge on gold (δ_{Au} = +0.724) is similar to that calculated for **3a** (δ_{Au} = +0.725) and both are smaller compared to that calculated for **3f** (δ_{Au} = +0.750). These results can be explained on the basis of the strong influence that the N ligand exerts on the overall polarization of the Au-F bond (δ_N = -0.509 for **3a** and = -0.525 for **3f**) and which is not reflected on the $^2J_{P-F}$. In fact, the overall distortion imposed by the sterics around the N atom compromises the overall σ donor ability of the bidentate ligand resulting in a more electropositive metal (δ_{Au} = +0.750) and thus a more polarized Au-F bond (δ_F = -0.594) in **3f**.[11]

Table 2. $^2J_{P-F}$ (Hz) and partial charges (δ) per atom for complexes **3a**, **3e** and **3f**. Natural Population Analysis based on the optimized structures obtained with B3LYP, 6-31G(d,p), Au (SDDAll), solvent (smd) =dichloromethane.

	3a	**3e**	**3f**
$^2J_{(P-F)}$	100.5	107.2	100.0
δ_{Au}	+0.725	+0.724	+0.750
δ_F	-0.590	-0.587	-0.594
δ_P	+1.194	+1.167	+1.167
δ_N	-0.509	-0.507	-0.525
δ_C	-0.177	-0.176	-0.162

The calculated Wiberg bond indexes (WBI) for Au-F bond are small (**3a**: 0.330, **3e**: 0.339 and **3f**·**SbF$_6$**: 0.321). Further, a local description of the occupancy in NBO confirms the polarized nature of the Au-F in these complexes.[11] Overall, and beyond small differences within the individual complexes, these results reveal a strong ionic character of the Au-F bond and strongly suggests a high nucleophilic and labile character for the fluoride ligands in these systems. We aimed to capitalize on these features in order to study C(sp^2)-C(sp) reductive elimination on gold(III). In contrast to the well-characterized C(sp^3)-C(sp^3), C(sp^2)-C(sp^2) and C(sp^2)-C(sp^3) reductive eliminations,[12] the analogous process for sp-hybridized systems has remained rather elusive. Further, while seminal work by Bourissou et al has demonstrated the utility of (P^N) ligands to study previously inaccessible oxidative addition processes and associated gold(I)/gold(III) catalytic cycles,[4f-h, 7] their utilization towards the study of the opposite process, i.e. reductive elimination, is yet to be reported.



Scheme 3. Reactivity of gold(III) fluorides **3** towards TMSCN (a,b) and alkynes (c,d) and subsequent C(sp^2)-C(sp) reductive elimination studies.

To our delight the reaction of **3a** with TMSCN at 25 °C produced quantitatively, 4-fluorobenzonitrile **6a** together with a new gold(I)cyano complex (**5**/Me$_3$SiSbF$_6$), whose structure could be confirmed by independent preparation through an alternative route.[8] Intrigued by these results, the same reaction was conducted at -60 ºC and monitored by *in situ* ^{19}F NMR.[8] In this case, a new complex could be detected and assigned as the expected arylgold(III) cyanide intermediate **4a**.[8,13] After warming up to 0 °C, **4a** evolved exclusively to **6a** (Scheme 3a). Temporal concentrations of cyano complex **4a** and product **6a** were calculated using 2-fluoronaphtalene as internal standard. The consumption of **4a** followed a clean irreversible first-order decay {-d[**4a**]/d*t* = k_1[**4a**]} up to conversions higher than 95%. The first-order rate constant (k_1) at 0 °C was calculated to be 5.98 x 10^{-4} s^{-1} while the rate of formation of **6a** matched with the rate of the consumption of **4a**,[8] suggesting that these two processes are intermolecularly connected. In the same way, the corresponding reaction of **3f** afforded **6a** quantitatively in less than 15 min at 0 °C,[8,14] which illustrates the effect of a more sterically hindered N on the rate of the C(sp^2)-C(sp)N reductive elimination. Similarly, complex **3c** reacted with TMSCN at 25 °C furnishing the corresponding arylgold(III) cyanide **4c** (Scheme 3a). **4c** was then converted to benzonitrile **6c** at 25 °C. In this case, the first-order rate constant (k_2) at 25 °C was calculated to be 4.45 x 10^{-4} s^{-1}. These results highlight the strong effect played by the (P^N) ligand in facilitating the formation of the new C(sp^2)-C(sp) bond,

as the analogous reductive elimination in the case of a monoligated (PPh_3)$AuArCN_2$ complex (Ar = 2,6-F_2-C_6H_3) proceeds exclusively under thermal conditions (above 60 ºC) over long periods of time.[15] As for the more electron-deprived complex **3f**, the C(sp^2)-C(sp) bond formation only occurred when the temperature is raised to 50 °C (Scheme 3b). In an analogous manner, the reaction of complexes **3a** and **3c** with methylpropiolate delivered the products of C(sp^2)-C(sp) reductive elimination **8a** and **8c** at ambient temperature in excellent yields. Interestingly, more electron-rich alkynes such as 1-ethynyl-(3,5-bistrifluoromethyl)benzene and phenylacetylene also delivered the corresponding cross-coupling products **9a** and **10a** in 53 and 72% yield, respectively (Scheme 3c). In this case, the quantitative formation (MeDalPhos)gold(I)-acetylide **7**/$HSbF_6$ after reaction completion could be again confirmed through its independent preparation by reaction of (MeDalPhos)gold(I) acetate with methylpropiolate.[8] These results are in line with those of the well-established C(sp^2)-C(sp^2) and C(sp^3)-C(sp^3) bond formation in phosphine ligated systems.[16]

Conclusion

Herein, we successfully synthesized, isolated and characterized a new family of stable bidentate (P^N)arylgold(III) fluoride complexes. Crystallographic and computational DFT analysis revealed a significant ionic character of the Au-F bond which correlates to the geometry distortion induced by the ligand. These complexes, featuring an unprecedented P-Au-F system, were able to activate C(sp) ligands such as methylpropiolate and TMSCN enabling the study of the corresponding C(sp^2)-C(sp) reductive elimination. This reaction proceeds under mild reaction conditions at higher rates than those reported for analogous phosphine-based monodentate systems, thus highlighting the potential of this work to develop and/or improve existing gold(I)/gold(III) catalytic methods for the cross coupling of C(sp^2)-C(sp) bonds.

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Keywords: gold(III) • fluoride • ligand exchange • reductive elimination

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[8] For further information and additional control experiments, see the Supporting Information. CCDC-2013400 (**2f**), 2013404 (**3a**), 2013404 (**3b**), 2013405 (**3d**), 2013406 (**3e**), contain the supplementary crystallographic data for this paper. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures

[9] The counterion did not influence the value of the $^{2}J_{P\text{-}F}$. Complex **3a**/BF_4 was prepared and its $^{2}J_{P\text{-}F}$ value (100.5 Hz) matches that obtained for the **3a**/SbF_6 analogue reported in Figure 1 and Table 1.

[10] For examples of study on the effect of phosphine sized on two-bond coupling see: a) For ^{13}C-Au-^{31}P: A. A. Isab, M. S. Hussain, M. N. Akhtar, M. I. M. Wazeer, A.R. Al-Arfaj, *Polyhedron* **1999**, *18*, 1401 – 1409; b) For ^{15}N-Pd-^{31}P: J. M. Dennis, N. A. White, R. Y. Liu, S. L. Buchwald, *J. Am. Chem. Soc.* **2018**, *140*, 4721.

[11] Different functionals and basis sets were tested in NPA analysis obtaining similar charge values. For further information, including NBO analysis on these systems, see the Supporting Information.

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[13] Complex **3d** was chosen to prepare **4d**-$^{13}C_{CN}$ given its reduced reactivity towards reductive elimination. When **3d** was treated with TMSCN-{$^{13}C_{\text{-}CN}$} at 25 °C, **4d**-$^{13}C_{CN}$ was formed displaying a characteristic strong *trans* $^{2}J(^{31}P\text{-}^{13}C)$ = 134.3 Hz that confirms the *trans* relative position of the CN and P ligand across the metal center.

[14] The rate constant was estimated to be $k > 4.6 \times 10^{-3}$ s^{-1} considering that the reaction reached up to 98.5% conversion in 15 min and it follows an irreversible first-order decay.

[15] A, Genoux, J. A. González, E. Merino, C. Nevado, *Angew. Chem. Int. Ed.* **2020**, *in print*. The rate constant k_1 (0 °C) was in the same range as the rate constant from gold(III) species bearing PPh_3 ligand at 100 °C ($k_{100\ °C} = 6.88 \times 10^{-4}$ s^{-1} ± 2.34×10^{-5} s^{-1}).

[16] Overall, the rates we observed are comparable to those previously reported for C(sp^3)-C(sp^3) reductive elimination in *cis*-$EtMe_2Au(PPh_3)$ and [*cis*-$(CH_3)_2Au(PPh_3)_2](PF_6)$ $k_{obs} \approx 10^{-5} – 10^{-3}$ s^{-1} at 70 °C (ref. 12a-d) as well as those reported for C(sp^2)-C(sp^2) in [*cis*-$(p\text{-}F\text{-}C_6H_4)_2Au(PPh_3)](Cl)$ $k_{obs} = 1.5 \times 10^{-4}$ s^{-1} at -52 °C (ref. 12f).

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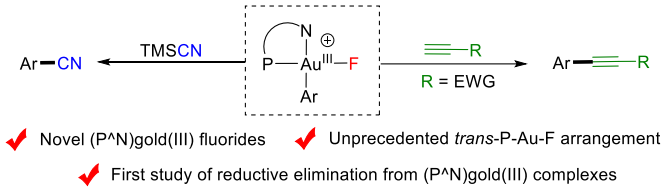

A new family of cationic bindenate (P^N)gold(III) fluoride complexes has been prepared and characterized. Ligand exchange with C(sp)-based nucleophiles enabled the first study of reactivity C(sp^2)-C(sp) reductive elimination on (P^N)gold(III) species.